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(12) UK Patent Application (19) GB (11) 2 095 114 A

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(21) Application No 8208099

(22) Date of filing 19 Mar 1982

(30) Priority data

(31) 8106046

(32) 24 Mar 1981

(33) France (FR)

(43) Application published

29 Sep 1982

(51) INT CL<sup>3</sup>

A01N 59/26 37/18

(52) Domestic classification

A5E 102 237 246 247 251

258 269 279 500 506 507

B

(56) Documents cited

GB 1525339

GB 1459539

(58) Field of search

A5E

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(54) Antifungal compositions based on phosphorous acid derivatives, and their application to the protection of plants

(57) Fungicidal compositions comprising a mixture of phosphites and of compounds of the N-(phenyl)-N-(acylmercaptoacetyl)-alaninate type and the use of these compositions in preventing or curing fungal diseases in plants, especially vines, are described.

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## SPECIFICATION

## Antifungal compositions based on phosphorous acid derivatives, and their application to the protection of plants

The present invention relates to fungicidal compositions based on metal phosphites, for the protection of plants, more especially vines, in particular against mildew, and also to a method for preventing or curing fungal diseases in plants, more especially vines, using these compositions. 5

Fungicidal compositions based on alkylphosphites which can be used, in particular, for protecting vines against mildew have been hitherto proposed (see French Patent Application No. 2,254,276). The active ingredient of these compositions is described as having a systemic action, compared with the earlier anti-mildew fungicides, i.e. from the point of application on the leaves, the active ingredient is transported by the sap to the other parts of the plant. 10

Experiments carried out in greater depth using these new fungicides on vines have made it possible to observe consistently that these alkyl-phosphites permit excellent protection of the vine leaves against mildew (*Plasmopara viticola*) during the first months of growth, but show a substantial decrease in activity when the leaves become senescent. Thus, as from the month of August in vines grown in France and at comparable stages in vines grown in other countries, it is possible to observe progressive attack by mildew of the oldest leaves, which are generally located at the base of the vine, whereas the remainder of the foliage, which has formed more recently, remains protected by virtue of the systemic action. 15

Certain fungicides of the family of the acylalanines are also known for their good preventive and curative action against vine mildew. A marketed product of this series, metalaxyl, gives a period of protection on vines which is substantially similar to that obtained with aluminium ethyl-phosphite. 20

One object of the present invention is to provide fungicidal compositions which are effective against mildew and, in particular, vine mildew.

Another object of the invention is to provide fungicidal compositions of systemic character. 25

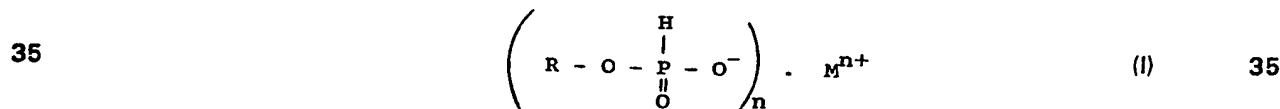
Another object of the invention is to provide fungicidal compositions having a prolonged action.

Another object of the invention is to provide fungicidal compositions which are capable of protecting vines even at the end of the season, including the oldest leaves.

Another object of the invention is to provide fungicidal compositions which are composed exclusively or almost exclusively of systemic fungicides. 30

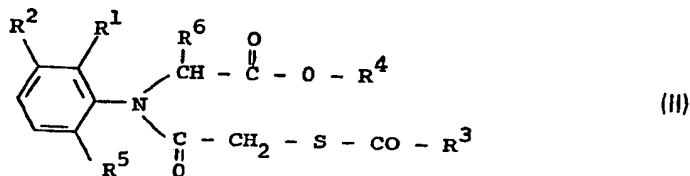
It has now been found that these objects can be achieved by virtue of the compositions according to the present invention.

Compositions according to the present invention comprise, as active ingredients, a mixture of 1) a phosphorous acid derivative of the general formula:



in which R is a hydrogen or sodium atom or an alkyl radical containing from 2 to 4 carbon atoms (when R is a hydrogen or sodium atom, M is preferably an alkali metal and n is preferably 1), M is an alkali metal atom, alkaline earth metal atom or aluminium atom, and n is an integer from 1 to 3, equal to the valency of M, and

2) a compound of the general formula: 40



in which R<sup>1</sup> and R<sup>5</sup>, which are identical or different, each represent the methyl radical or the ethyl radical, R<sup>2</sup> is a hydrogen or chlorine atom, R<sup>3</sup> is an alkyl radical containing from 1 to 12 carbon atoms, R<sup>4</sup> is an alkyl radical containing from 1 to 4 carbon atoms and R<sup>6</sup> is a hydrogen atom or the methyl radical. 45

The formula (I) of the first compound of the mixture has been represented in the usual diagrammatic way; it must be specified, however, that the R—O bond can in fact be either a normal valence bond, especially if R is an alkyl radical, or a mainly ionic bond, especially if R is the sodium atom.

Furthermore, it is possible to use either a single compound of the formula (I) or a mixture of compounds which are different but have the same general formula (I); likewise, in the case of the 50

compound of formula (II), it is possible to use a mixture of two compounds having different individual formulae.

The compounds of general formula (II) are derivatives or homologues of the N-(phenyl)-N-(acylmercaptoacetyl)-alaninates.

5 Particularly preferred mixtures are those in which:

the compound of general formula (I) is aluminium ethyl-phosphite or calcium ethyl-phosphite or a sodium phosphite (monosodium or disodium phosphite), and

the compound of general formula (II) is such that  $R^1=R^5$ =methyl,  $R^2=Cl$  or H,  $R^3$ =methyl,  $R^4$ =methyl or ethyl and  $R^6$ =methyl.

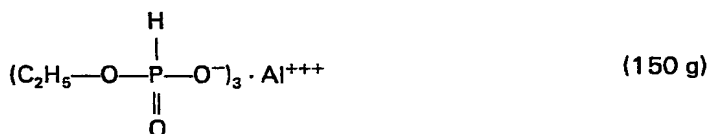
10 The proportion of the constituents in the mixture can vary within wide limits. The proportions by weight of the constituents of the formula (I) and (II) in the mixture are generally between 1/1 and 30/1 and preferably between 5/1 and 15/1 (these values denote the weight ratio of the active ingredients of the formula (I) relative to the active ingredients of the formula (II)). If at least some of the constituents of the formula (I) are such that R is the hydrogen or sodium atom, preferably at least 50% by weight of the compounds of the formula (I) is such that R represents an alkyl radical.

15 The mixtures according to the invention can be prepared as a formulation which is ready for use, or prepared extemporaneously.

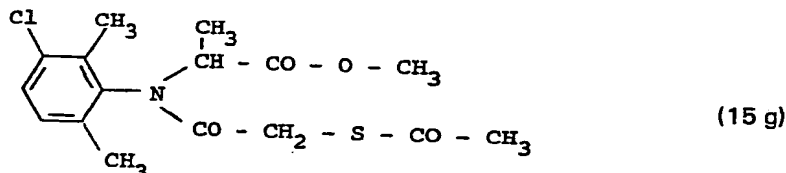
The Example which follows, which is given without implying a limitation, illustrates the invention and shows how it can be put into practice.

## 20 Example

A mixture of



and the compound of the formula:



25 is prepared.

This mixture, formulated as hereinafter described, is used *in vivo* against *Plasmopara viticola* on vine plants (curative treatment).

Vine plants (GAMAY variety), cultivated in pots, are treated on both sides of their leaves by being sprayed with an aqueous emulsion containing the active ingredients to be tested; first an emulsion consisting of the mixture of active ingredients to be tested (40 mg), water (40 cc) and Tween 80 (surface-active agent consisting of the oleate of an ethylene oxide/sorbitol condensate; 0.02 cc), is prepared.

30 The emulsion, made up in this way, is diluted with water to give a spraying emulsion in which the concentration of active ingredients to be tested is equal to 165 mg/litre (150 mg/litre of the first compound and 15 mg/litre of the second compound). The spraying is carried out under conditions such that the spraying of an emulsion having a concentration equal to 1 g/litre corresponds to the application of about 2 micrograms of active ingredients per cm<sup>2</sup> of surface area of the plant leaf.

35 48 Hours before the active ingredients were sprayed, the plants had been contaminated by being sprayed, on the underside of the leaves, with an aqueous suspension of fungus spores (about 80,000 units/cc). The pots had then been placed for 48 hours in an incubation cell at 100% relative humidity and at 20°C.

The plants are checked 9 days after infestation, i.e. 7 days after the treatment by spraying with active ingredients.

45 According to this test, the mixture used in the experiments provided total protection of the plants at a dose of 165 mg/litre of mixture of active ingredients. Similar tests using doses of 110 and 11 mg/litre of the mixture also gave total protection of the plant.

Application of the same mixtures to vine plants in the open air also makes it possible to provide protection both for the recently formed leaves and for the old leaves at the base of the vines.

50 The experiments carried out with the mixtures according to the invention show noteworthy fungicidal properties, which are not obvious, especially on fungi of the phycomycetes type (mildew), and also the absence of phytotoxicity in these mixtures; their high activity, even at low doses, is quite

remarkable. These mixtures can therefore be used, in both a preventive and a curative capacity, for combatting fungal diseases in plants in general, and in particular in vine, tobacco, hop and tomato plants.

For their use in practice, the active ingredients of the compositions according to the invention are rarely employed by themselves. Most frequently, they form part of more complex compositions. Accordingly, compositions according to the invention, which can be used for preventing or curing fungal diseases in plants, contain compounds according to the invention, such as described above, as active ingredients, in association with solid or liquid carriers which are acceptable in agriculture, and/or surface-active agents which are also acceptable in agriculture. In particular, the customary inert carriers and the customary surface-active agents can be used.

These compositions can also contain all kinds of other ingredients such as e.g. protective colloids, adhesives, thickeners, thixotropic agents, penetrating agents, stabilisers, sequestering agents and the like, as well as other known active ingredients having pesticidal properties (in particular insecticidal or fungicidal properties) or having properties which promote plant growth (in particular fertilisers) or having properties which regulate plant growth. More generally, the active ingredients of the compositions according to the invention can be used in association with all of the solid or liquid additives used in the usual formulation techniques.

The use doses of the active ingredients of the compositions according to the invention can vary within wide limits, depending in particular on the virulence of the fungi and on the climatic conditions; however, the compositions according to the invention are most commonly applied to the plants at a rate of 0.5 to 5 kg of active ingredients per hectare of crop, and preferably at a rate of 1 to 3.5 kg/ha.

In general, the compositions for agricultural use, according to the invention, which comprise compounds according to the present invention as active ingredients in association with a solid or liquid carrier which is acceptable in agriculture and/or a surface active agent which is acceptable in agriculture, contain from 0.1 to 95% (by weight) of active ingredients.

As regards the compositions suitable for storage and transportation (also called formulations), these more advantageously contain from 10 to 95% (by weight) of active ingredients.

The active ingredients of the compositions according to the invention are generally used in association with solid or liquid carriers and, if appropriate, surface-active agents.

In the present specification, the term "carrier" denotes an organic or inorganic, natural or synthetic material with which the active ingredient is associated in order to facilitate its application to the plant, to seeds or to the soil. This carrier is therefore generally inert and it must be acceptable in agriculture, in particular on the plant treated. The carrier can be solid (clays, natural or synthetic silicates, silica, resins, waxes, solid fertilisers or the like) or liquid (water, alcohols, ketones, petroleum fractions, aromatic or paraffinic hydrocarbons, chlorohydrocarbons, liquefied gases or the like).

The surface-active agent can be an emulsifying, dispersing or wetting agent of the ionic or non-ionic type. Examples which may be mentioned are salts of polyacrylic acids, salts of lignosulphonic acids, salts of phenolsulphonic or naphthalenesulphonic acids, polycondensates of ethylene oxide with fatty alcohols, fatty acids or fatty amines and substituted phenols (in particular alkylphenols or arylphenols), salts of sulphosuccinic acid esters, taurine derivatives (in particular alkyl-taurates) and phosphoric acid esters of condensates of ethylene oxide with alcohols or phenols. The presence of at least one surface-active agent is generally essential if the active ingredients and/or the inert carrier are not soluble in water and if the vehicle of application is water.

For their application, the compositions according to the invention are generally in a fairly wide variety of solid or liquid forms.

As forms of solid compositions, there may be mentioned dusting powders or sprinkling powders (with an active ingredient content which can range up to 100%).

As forms of liquid compositions or compositions which are to be made up into liquid compositions on application (the latter being called "slurries"), there may be mentioned solutions, in particular water-soluble concentrates, emulsifiable concentrates, emulsions, suspension concentrates, aerosols, wettable powders (or spraying powders) and pastes.

The emulsifiable or soluble concentrates most frequently comprise 10 to 80% of active ingredients, and the emulsions or solutions which are ready for application contain 0.01 to 20% of active ingredients. In addition to the solvent, and where necessary, the emulsifiable concentrates can contain 2 to 20% of suitable additives such as stabilisers, surface-active agents, penetrating agents, corrosion inhibitors, dyestuffs and adhesives. The composition of some concentrates are now given as Examples:

#### Emulsifiable concentrate:

60	active ingredients	400 g/litre	
	alkali metal dodecylbenzenesulphonate	24 g/litre	
	10:1 ethylene oxide/nonylphenol condensate	16 g/litre	60
	cyclohexanone	200 g/litre	
	aromatic solvent	q.s.p.	
		1 litre	

Another formulation of an emulsifiable concentrate uses the following constituents:

	active ingredients	250 g	
	epoxidised vegetable oil	25 g	
5	mixture of an alkylarylsulphonate and a polyglycol ether of fatty alcohols	100 g	5
	dimethylformamide	50 g	
	xylene	575 g	

Starting from these concentrates, emulsions of any desired concentration, which are particularly suitable for application to the leaves, can be obtained by dilution with water.

- 10 The suspension concentrates, which can also be applied by spraying, are prepared so as to give a stable fluid product which does not form a deposit, and they usually contain from 10 to 75% of active ingredients, from 0.5 to 15% of surface-active agents, from 0.1 to 10% of thixotropic agents, from 0 to 10% of suitable additives such as anti-foam agents, corrosion inhibitors, stabilisers, penetrating agents and adhesives, and, as the carrier, water or an organic liquid in which the active ingredient is sparingly soluble or insoluble; certain organic solids, or inorganic salts, can be dissolved in the carrier in order to assist in preventing sedimentation or to act as anti-freeze agents for the water. 15

- The wettable powders (or spraying powders) are usually prepared so as to contain 20 to 95% of active ingredients, and they usually contain, in addition to the solid carrier, from 0 to 5% of a wetting agent, from 3 to 10% of a dispersing agent and, where necessary, from 0 to 10% of one or more stabilisers and/or other additives such as penetrating agents, adhesives, anticaking agents, dyestuffs, antiflocculants or the like. 20

Various compositions of wettable (or spraying) powders are now given as Examples:

	active ingredients	50%	
25	calcium lignosulphonate (deflocculant)	5%	
	isopropyl-naphthalenesulphonate (anionic wetting agent)	1%	25
	anti-caking silica	5%	
	kaolin (filler)	39%	

Another composition of a 70% strength spraying powder uses the following constituents:

30	active ingredients	700 g	30
	sodium dibutyl-naphthylsulphonate	50 g	
	3:2:1 naphthalenesulphonic acid/phenol-sulphonic acid/formaldehyde condensate	30 g	
35	kaolin	100 g	
	Champagne chalk	120 g	35

Another composition of a 40% strength spraying powder uses the following constituents:

	active ingredients	400 g	
	sodium lignosulphonate	50 g	
40	sodium dibutyl-naphthalenesulphonate	10 g	
	silica	540 g	40

Another composition of a 25% strength spraying powder uses the following constituents:

	active ingredients	250 g	
	calcium lignosulphonate	45 g	
45	mixture of equal parts by weight of Champagne chalk and hydroxyethylcellulose	19 g	45
	sodium dibutyl-naphthalenesulphonate	15 g	
	silica	195 g	
	Champagne chalk	195 g	
	kaolin	281 g	

- 50 Another composition of a 25% strength spraying powder uses the following constituents: 50

	active ingredients	250 g	
	isooctylphenoxy-polyoxyethylene-ethanol	25 g	
55	mixture of equal parts by weight of Champagne chalk and hydroxyethylcellulose	17 g	55
	sodium aluminosilicate	543 g	
	kieselguhr	165 g	

Another composition of a 10% strength spraying powder uses the following constituents:

	active ingredients	100 g	
	mixture of sodium salts of saturated fatty acid sulphates	30 g	
5	naphthalenesulphonic acid/formaldehyde condensate	50 g	5
	kaolin	820 g	

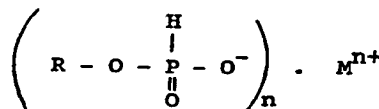
To obtain these spraying powders or wettable powders, the active ingredients are intimately mixed, in suitable mixers, with the additional substances, and the mixture is ground in mills or other suitable grinders. This gives spraying powders of advantageous wettability and suspendability; they can be suspended in water at any desired concentration, and this suspension can be used very advantageously, in particular for application to the leaves of the plants.

In place of the wettable powders, it is possible to produce pastes. The conditions and modes of production and use of these pastes are similar to those of the wettable powders or spraying powders. As already stated, the aqueous dispersions and aqueous emulsions, e.g. compositions obtained by diluting, with water, a wettable or spraying powder or an emulsifiable concentrate according to the invention, are included in the general scope of the present invention. The emulsions can be of the water-in-oil or oil-in-water type and they can have a thick consistency such as that of a "mayonnaise".

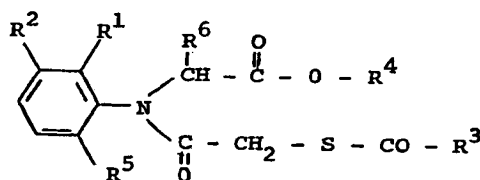
The compositions according to the invention can also be used in the form of dusting powders, for example a composition comprising 50 g of active ingredients and 950 g of talc, or a composition comprising 20 g of active ingredients, 10 g of finely divided silica and 970 g of talc; these constituents are mixed and ground and the mixture is applied by dusting.

#### Claims

1. A composition for preventing or curing fungal diseases in plants which comprises a mixture of a compound of the general formula:



in which R is a hydrogen or sodium atom or an alkyl radical containing from 2 to 4 carbon atoms, M is an alkali metal atom, alkaline earth metal atom or aluminium atom, and n is an integer from 1 to 3, equal to the valency of M, and a compound of the general formula:



in which R<sup>1</sup> and R<sup>5</sup>, which are identical or different, each represent the methyl radical or the ethyl radical, R<sup>2</sup> is a hydrogen or chlorine atom, R<sup>3</sup> is an alkyl radical containing from 1 to 12 carbon atoms, R<sup>4</sup> is an alkyl radical containing from 1 to 4 carbon atoms, and R<sup>6</sup> is a hydrogen atom or the methyl radical.

2. A composition according to claim 1 in which M is an alkali metal atom and n is 1 if R is a hydrogen or sodium atom.

3. A composition according to claim 1 or 2 in which the compound of formula I is aluminium ethylphosphite, calcium ethyl-phosphite, a monosodium phosphite or disodium phosphite, R<sup>1</sup> and R<sup>5</sup> are each the methyl radical, R<sup>2</sup> is the hydrogen or chlorine atom, R<sup>3</sup> is the methyl radical, R<sup>4</sup> is a methyl or ethyl radical and R<sup>6</sup> is the methyl radical.

4. A composition according to any one of the claims 1 to 3 in which the proportion by weight of the constituents of the mixture of formula I, relative to the constituents of formula II, is between 1/1 and 30/1.

5. A composition according to any one of claims 1 to 4 in which the proportion by weight of the constituents of formula I, relative to the constituents of formula II, is between 5/1 and 15/1.

6. A composition according to any one of claims 1 to 5 in which, amongst the active ingredients of formula I, at least 50% by weight thereof are such that R is an alkyl radical in their formulae.

7. A composition according to any one of claims 1 to 6 which comprises as active ingredient a mixture of a compound of formula I and a compound of formula II as defined in any one of claims 1 to 6

in association with a solid or liquid carrier which is acceptable in agriculture and/or a surface active agent which is acceptable in agriculture.

8. A composition according to claim 7 which is in the form of a wettable powder or an aqueous suspension containing 0.1 to 95% by weight of active ingredients.

5 9. A composition for preventing or curing fungal diseases in plants substantially as hereinbefore described. 5

10. A composition for preventing or curing fungal diseases in plants substantially as hereinbefore described in the Examples.

10 11. A method for preventing or curing fungal diseases in plants which comprises applying an effective amount of a composition according to any one of claims 1 to 10 to the plants. 10

12. A method according to claim 11 which comprises applying a composition according to one of claims 1 to 10 at a rate of 0.5 to 5 kg/ha of active ingredient.

13. A method according to claim 11 which comprises applying a composition according to one of claims 1 to 10 at a rate of 1 to 3.5 kg/ha of active ingredient.

15 14. A method according to any one of claims 11 to 13 in which the plants are vines, tobacco, hops or tomatoes. 15

15. A method according to any one of claims 11 to 13 in which the plants are vines.

16. A method according to any one of claims 11 to 15 in which the plants are vines and the fungal disease is mildew caused by *Plasmopara viticola*.

20 17. A method for preventing or curing fungal diseases in plants substantially as hereinbefore described. 20

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1982. Published by the Patent Office,  
25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

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